

# SPECTRAL EMISSIVITY OF DIELECTRIC OXIDES, BELOW AND ABOVE THE MELTING POINT<sup>1</sup>

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## ABSTRACT

Infrared emission spectroscopy has been used to study melting and premelting effects of materials with a high melting temperature. The normal spectral emissivity of very pure MgO and Al<sub>2</sub>O<sub>3</sub> single crystals was measured up to the temperature of 2600 K over the frequency range from 350 cm<sup>-1</sup> up to 6000 cm<sup>-1</sup>. The anomalous increase of the emissivity which begins several hundred degrees below the melting point within the transparency region, typically from 3500 cm<sup>-1</sup> to 6000 cm<sup>-1</sup>, was interpreted as premelting effects. For the first time such spectra could have been completely fitted thanks to a dielectric function model. The results indicate that a simple Debye relaxation term is needed to perfectly fit this increase of the emissivity. The oscillator strength of the Debye term appears to be thermally activated with similar activation energy for MgO and Al<sub>2</sub>O<sub>3</sub>. The relaxation phenomenon exhibits a very high characteristic relaxation frequency. It is concluded that such an absorption level within the transparency region is due to electronic phenomena.

KEY WORDS: dielectric function model, dielectric oxides, FTIR spectroscopy, melting, normal spectral emissivity, premelting effects.

## 1. INTRODUCTION

The spectral emissivity appears to be a valuable quantity to study melting and premelting effects of semitransparent materials with a high melting temperature and seems to be the best way to reach the optical parameters in the solid state as well as in the liquid state. Yet the studies over a wide frequency range and a wide temperature range are very scarce in the literature, even in the case of very extensively studied oxides such as corundum and magnesia. In a previous work [1] we took advantage of the emissometer developed at the laboratory to study the normal spectral emissivity of MgO and Al<sub>2</sub>O<sub>3</sub> single crystals measured over the frequency range from 350 cm<sup>-1</sup> up to 6000 cm<sup>-1</sup> (i.e. 2 μm to 28 μm) and with increasing temperature up to 2600 K. The anomalous increase of the emissivity within the transparency region, typically up to 3500 cm<sup>-1</sup>, several degrees before melting was analyzed through the absorption

coefficient and interpreted as premelting effects due to the mobility of some entities such as ions or vacancies.

In this paper we complete this work and propose a new way to totally simulate the emissivity spectra thanks to a dielectric function model. As far as we know this is the first time that emissivity spectra of dielectric compounds are directly and completely fitted in such a way and over such a wide frequency and temperature range, up to the liquid state. In this study we are still particularly focusing on the anomalous increase of the emissivity observed within the transparency region (typically from 3500 cm<sup>-1</sup> to 5500 cm<sup>-1</sup>, i.e. 2 μm to 3 μm) before melting. The simulation is fulfilled thanks to a simple Debye relaxation term with very high values of characteristic frequency. This approach is expected to extend to other oxide materials.

## 2. METHOD

### 2.1. Emissivity measurements

The experimental method for measuring the spectral emissivity  $\varepsilon(\sigma, T)$  was already published in [1,2]. The experimental device is based on a Bruker IFS 113V FTIR spectrometer, a sample chamber, a reference blackbody furnace and a 10.6 μm CO<sub>2</sub> laser. The spectrometer allows flux measurements over a wide frequency range, from 10 cm<sup>-1</sup> to 12 000 cm<sup>-1</sup>. The CO<sub>2</sub> laser heating allows reaching the high melting temperatures of most of the oxides, typically up to 2600 K.

The FTIR spectrometer is used as a pyrometer for the temperature measurement by using the Christiansen's point. The latter is the wave number at which the spectral emissivity is equal to one. This particular wave number is a characteristic of most of heteropolar dielectric materials and then of all the oxides we are studying.

### 2.2. Simulation

We carried out emissivity measurements within the spectral range from 350 cm<sup>-1</sup> up to 6 000 cm<sup>-1</sup>. Each spectrum can be divided into three regions: the phonon or opaque region up to the Christiansen's point, the multiphonon or semi-transparent region at higher frequencies and the transparency region typically from 3 500 cm<sup>-1</sup>. Our approach is to fit the measured emissivity spectra directly thanks to a dielectric function model. The application of classical-oscillator theory to the analysis of phonon absorptions in the case of infrared reflectivity spectra has been extensively reviewed and discussed [3]. The problem is the same in the case of emissivity spectra since

$$\varepsilon(\sigma, T) = 1 - R(\sigma, T) \quad (1)$$

within the opaque region. In the above equation,  $\varepsilon$  is the spectral emissivity,  $R$  the reflectivity,  $\sigma$  the wave number and  $T$  the temperature.

But in our case we have to take into account all other absorption phenomena which contribute to the dielectric function within the considered spectral range (from 350 cm<sup>-1</sup> up to 6 000 cm<sup>-1</sup>) and particularly the multiphonon processes from which the transparent edge in the spectra originate. To achieve that we used the following semi-quantic dielectric function model

$$\tilde{\varepsilon}_{\sigma} = \varepsilon_{\infty} + \sum_{j=1}^n \Delta\varepsilon_j \frac{\Omega_{jTO}^2(\sigma, T)}{\Omega_{jTO}^2(\sigma, T) - \sigma^2 - i\gamma_j(\sigma, T)} + \frac{ds}{1 - i\sigma\tau} \quad (2)$$

where  $\tilde{\varepsilon}_{\sigma}$  is the dielectric function,  $\Omega_{jTO}$  is the wavenumber of the  $j^{\text{th}}$  transverse optical mode,  $\Delta\varepsilon_j$  the oscillator force of the  $j^{\text{th}}$  oscillator,  $\gamma_j$  the damping function,  $ds$  the dielectric strength of the Debye relaxation term and  $\tau$  the “relaxation time” (here in cm). In this model the classical damping function is replaced by a quantity called the self-energy so that  $\Omega_{jTO}$  and  $\gamma_j$  are frequency and temperature dependent and can accounts for all anharmonic couplings which relax the  $j$ -mode [3,4,5]. In practice we directly adjust the parameters  $\varepsilon_{\infty}$ ,  $\Delta\varepsilon_j$ ,  $\Omega_{jTO}$ ,  $\gamma_j$ ,  $ds$  and  $\tau$  in the powerful curve fitting program named FOCUS developed by D.D.S. Meneses [6]. The Debye relaxational term was introduced to fit the spectra within the transparency region and will be discussed below.

$\gamma_j$  is a sum of different functions and can be written as follow

$$\gamma_j(\sigma) = \sum_i L_i(\sigma) + \sum_i G_i(\sigma) + \sum_i L'_i(\sigma) \quad (3)$$

where  $L_i(\sigma)$  is a lorentzian function,  $G_i(\sigma)$  a gaussian function and  $L'_i(\sigma)$  a generalized Laplace function given by the following expression

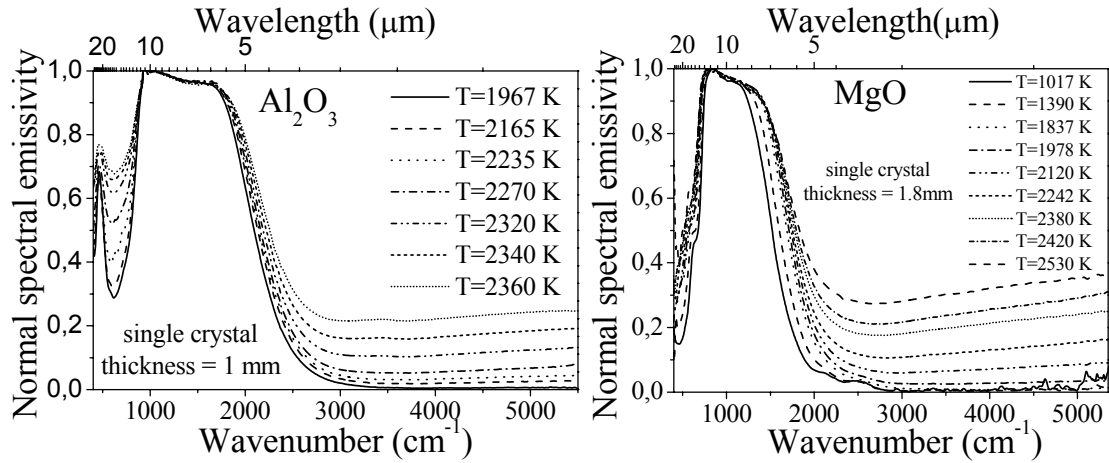
$$L'_i(\sigma) = \begin{cases} Ae^{-p_1(\sigma-\sigma_0)} & \sigma \geq \sigma_0 \\ Ae^{-p_2(\sigma-\sigma_0)} & \sigma < \sigma_0 \end{cases} \quad (4)$$

where  $A$ ,  $p_1$  and  $p_2$  are constants.

### 3. RESULTS

We measured the normal spectral emissivity of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  single crystals 1 mm and 1.8 mm thick respectively. The purity of these samples was greater than 99.9%. The  $\text{Al}_2\text{O}_3$  samples were cut normally to the c-axis. The melting temperatures of corundum and magnesia are 2327 K and 3073 K respectively. The melting temperature of magnesia could not have been reached since our laser is not powerful enough. In the case of  $\text{Al}_2\text{O}_3$  the spectra were obtained a few degrees beyond the melting point.

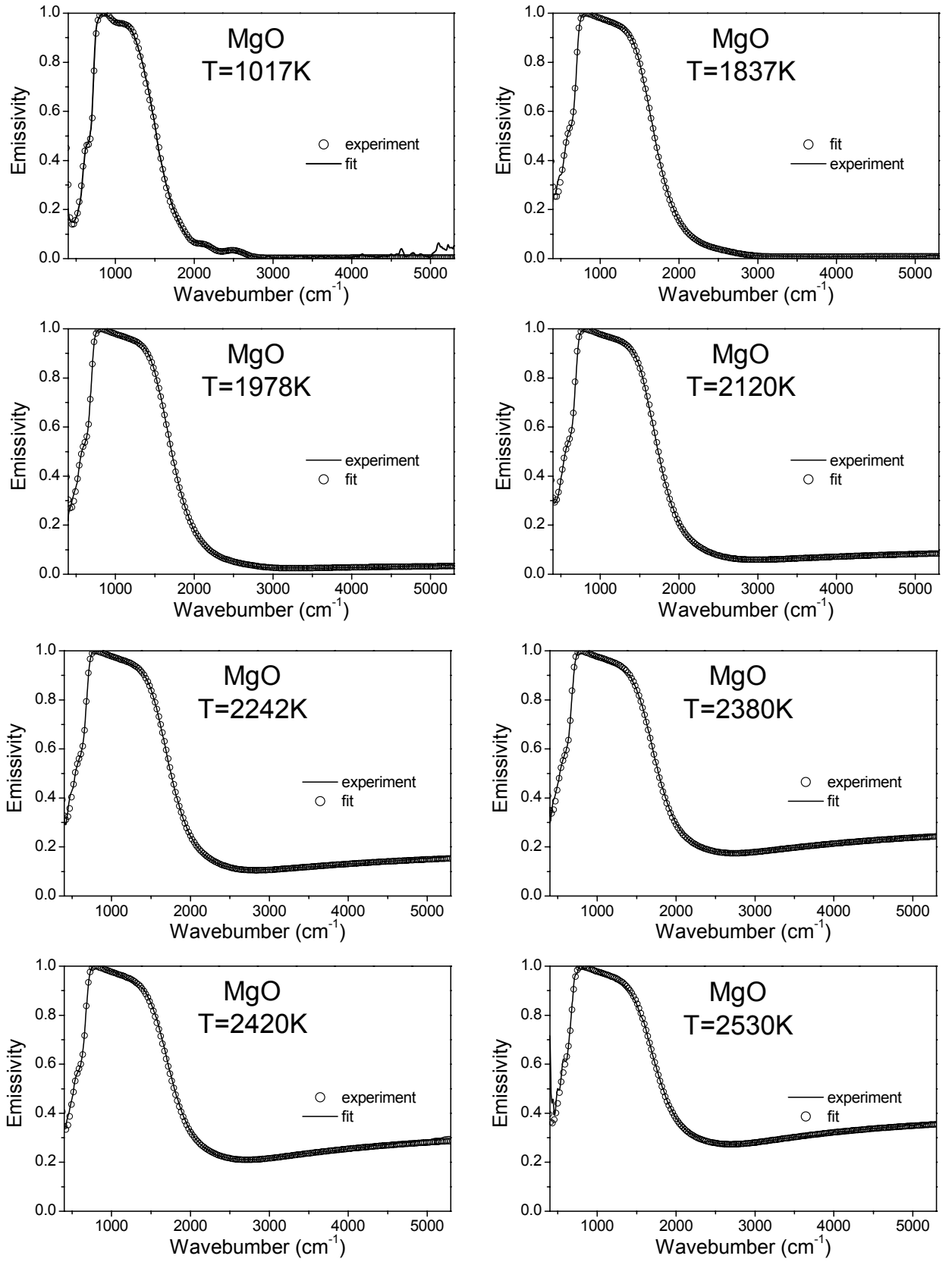
Measured normal spectral emissivities for  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in the spectral range from  $350 \text{ cm}^{-1}$  up to  $6000 \text{ cm}^{-1}$  are given in the figure 1. Between  $3500 \text{ cm}^{-1}$  and  $6000 \text{ cm}^{-1}$  the material is expected to remain transparent that is to say  $\varepsilon(\sigma, T) \approx 0$  whatever the temperature  $T$  is. As one can see there is a significant increase of  $\varepsilon(\sigma, T)$  with increasing temperature which begins about a hundred degrees before melting in the case of  $\text{Al}_2\text{O}_3$  and several hundred degrees in the case of  $\text{MgO}$ .



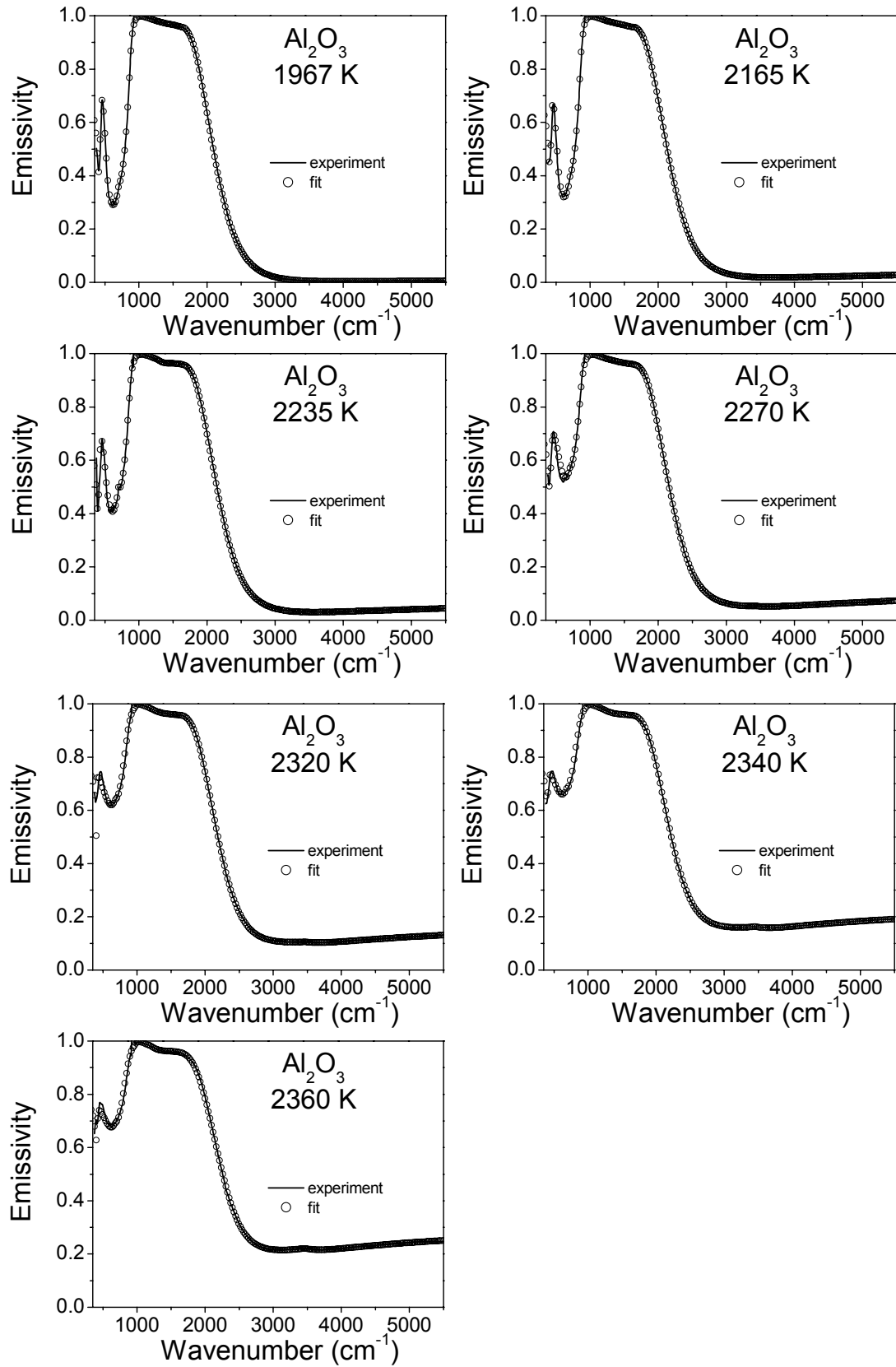
**Fig. 1.** Temperature dependence of the normal spectral emissivity of alumina and magnesia.

The spectra of the figure 1 were fitted with the FOCUS software which uses the dielectric function model of equation (2). The results are shown in figures 2 and 3. It appears that the model fits the spectra very well. The figure 4 exhibits the evolution with the temperature of the damping functions used in the model to correctly fit the spectra of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . In the case of  $\text{Al}_2\text{O}_3$  four generalized Laplace functions and one gaussian function were needed to reproduce each spectrum. In the case of  $\text{MgO}$  one lorentzian function, one generalized Laplace function and two gaussian functions were necessary. The parameters of the Debye relaxation term used in the model of equation (2) to fit the spectra within the transparency region are plotted versus the temperature in Fig. 5. The parameter  $ds$  appears to be thermally activated for  $\text{Al}_2\text{O}_3$  as well as for  $\text{MgO}$  and exhibits two different behaviors in the case of  $\text{Al}_2\text{O}_3$ : the first one up to about one hundred degree before the melting point and the second one beyond. The activation energies are 1.12 eV and 0.99 eV for  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  respectively before melting in both cases. The parameter  $\tau$  appears to vary linearly with temperature from 1 900 to 2 000 K and to remains constant at lower temperature. The values of  $\tau$  appears to be similar for  $\text{Al}_2\text{O}_3$  and for  $\text{MgO}$ .

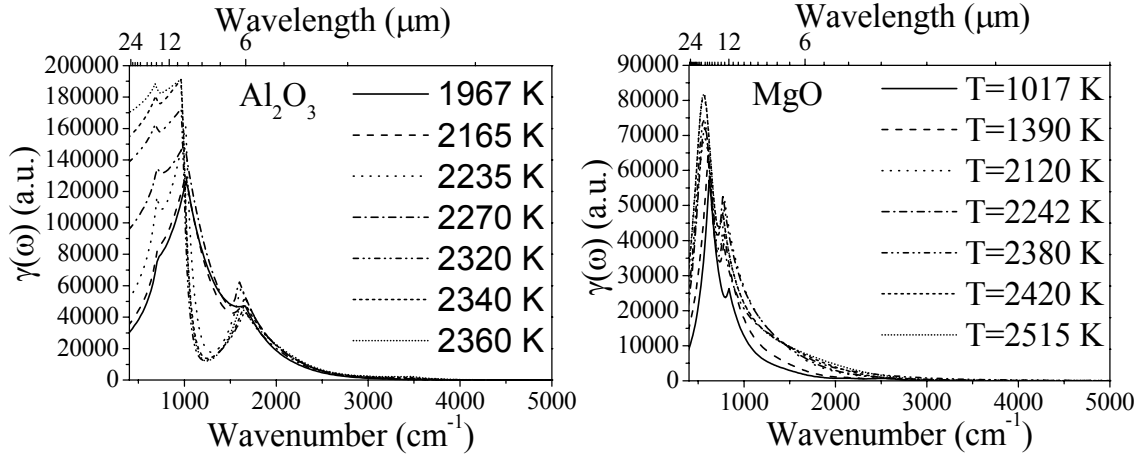
Even though  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  single crystals have been extensively studied for a long time such results from normal spectral emissivities have been obtained for the first time.



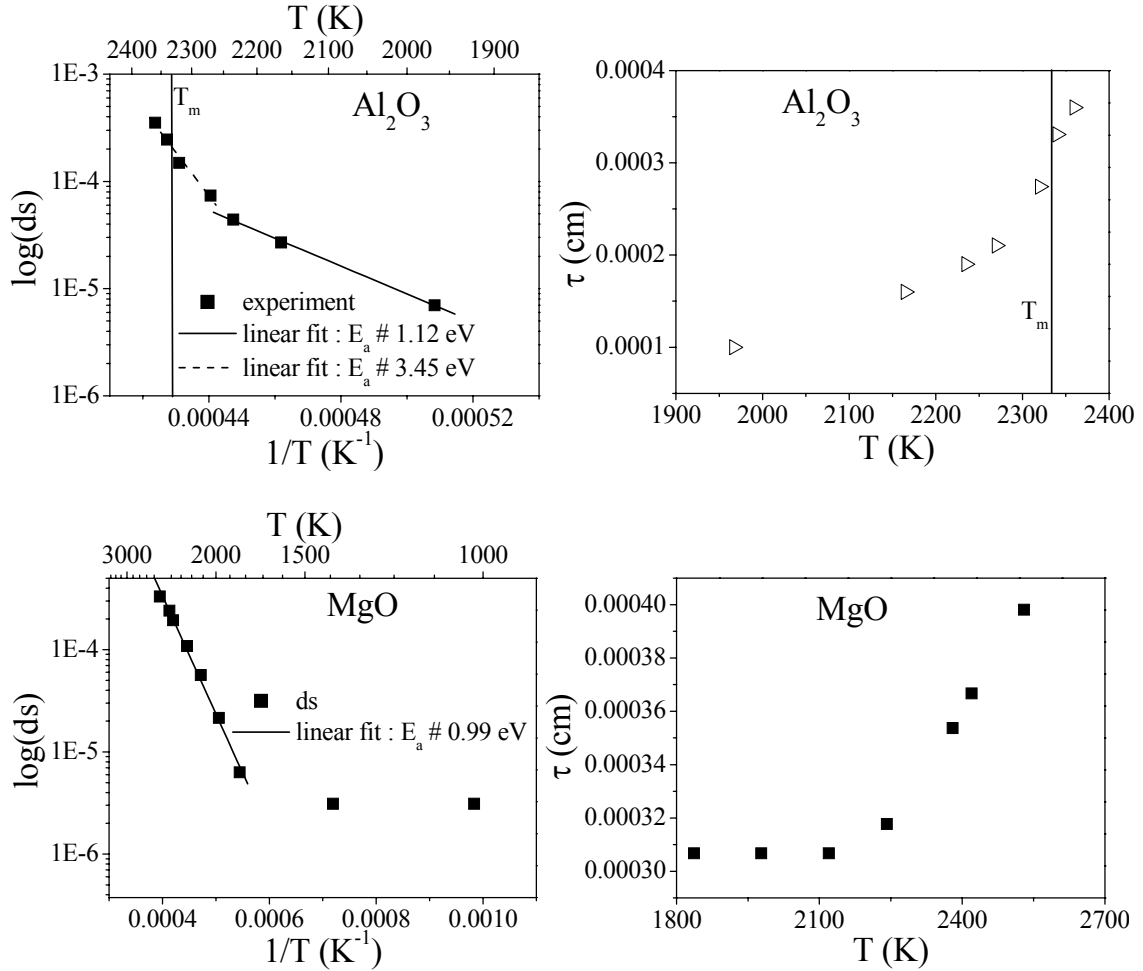
**Fig. 2.** Simulation of the measured emissivity spectra of MgO with the dielectric function model of equation (2).



**Fig. 3.** Simulation of the measured emissivity spectra of  $\text{Al}_2\text{O}_3$  with the dielectric function model of equation (2).



**Fig. 4.** Damping function used in the model of equation (2) to fit the measured spectra of Fig. 1.



**Fig. 5.** Parameters of the Debye relaxation term used to fit the transparent region of the measured emissivities of Fig. 1.

#### 4. DISCUSSION

In this work we propose a new approach in studying infrared absorption mechanisms of dielectric oxides at high temperature and over a wide frequency range. As far as we know only Sova *et al* [7] and Thomas *et al* [8] carried out similar experiments and fitted some emissivity spectra of  $\text{Al}_2\text{O}_3$  single crystals. Nevertheless on the one hand their approach is rather different since it is based on Kramers-Kronig relation and on the other hand the temperature of their emissivity spectra never exceeds 2 000 K so that no anomalous increase of the emissivity beyond 3 500  $\text{cm}^{-1}$  is observed and discussed. Thus even if the reliability of our experimental results was demonstrated many years ago [2], the lack of available literature data prevents us from any comparison of our analysis.

As previously mentioned in part 2.2 each emissivity spectrum can be divided into three regions which originate from three different absorption mechanisms. It is shown that the dielectric function model of equation (2) allows fitting these three regions very well. The results of the figure 4 confirm that the damping function of broad and non symmetric phonon band is highly frequency and temperature dependant and pilots the multiphonon absorptions entirely. Indeed the transparent edge in the emissivity spectra, typically from 1 000  $\text{cm}^{-1}$  up to 3 000  $\text{cm}^{-1}$ , is entirely fitted by adjusting the parameters of the damping function. As a consequence the temperature dependence of this transparency edge is directly explained by the evolution versus the temperature of the corresponding damping function. In the case of MgO there is only one phonon that is infrared active. But in the case of  $\text{Al}_2\text{O}_3$  four infrared modes are infrared active at 385, 442, 569 and 635  $\text{cm}^{-1}$  at room temperature [9]. Since the broad band in the phonon spectrum is due to the mode at 569  $\text{cm}^{-1}$ , the multiphonon processes are piloted by its damping function and not by the phonon of highest energy as expected [3]. The damping function seems also to exhibit always a predominant peak the slopes of which pilot the evolution with temperature of the corresponding phonon at low frequency and the slope of the transparent edge at high frequency. Finally the results of the figure 4 also show that the multiphonon processes that can theoretically occur far away from the last phonon mode are only significant up to 3 500  $\text{cm}^{-1}$ . It is to be theoretically possible to identify to which phonon couplings the different peaks in the damping function correspond. This point will not be discussed in this paper.

We are now particularly focusing on the analysis of the anomalous increase of the emissivity within the transparency region, typically above 3 500  $\text{cm}^{-1}$ . It is well known that absorptions due to impurities can occur within this spectral range [10] but in such pure crystals nothing can *a priori* explain such high absorption levels. In a previous contribution [1] we supposed that it was due to the mobility of some entities such as ions or vacancies. The new results presented in this paper allow us to precise this conclusion. We fitted the emissivity spectra within the transparency region thanks to a simple Debye relaxation term characterized by its two parameters  $ds$  and  $\tau$  in equation (2). At first since the dielectric strength  $ds$  appears to be thermally activated with similar activation energy before melting in the case of  $\text{Al}_2\text{O}_3$  and in the case of MgO as well, we conclude that the anomalous increase of the emissivity within the transparency region originates from the same phenomenon in both cases. Moreover the two thermally activated behaviors observed in the case of  $\text{Al}_2\text{O}_3$  confirm that this compound exhibits premelting effects over a premelting range of about one hundred degrees. Nevertheless such a relaxation term is expected with a low characteristic frequency ( $10^6$  Hz that is to



say  $3.10^{-3} \text{ cm}^{-1}$ ) [11]. In this work the values of  $\tau$  are included between  $10^{-4}$  and  $4.10^{-4}$  cm that is to say 2 500 and 10 000  $\text{cm}^{-1}$ . It has been shown that  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$  respectively, and  $\text{O}^{2-}$  ions were responsible for ionic conductivity in  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  respectively [12,13]. The mobility of such heavy entities does not agree with a relaxation phenomenon with such high characteristic frequencies. We then suppose that it can only be due to electrons, to a phenomenon which occur at higher frequency such as electronic transitions. Besides the different activation energies of 0.99, 1.12 and 3.45 eV found in this work are quite similar to energies of electronic level populating.

## 5. CONCLUSION

A new approach to analyze the emissivity spectra of semitransparent materials with a high melting temperature, below and above the melting point, has been introduced. For the first time the normal spectral emissivity of  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  single crystals were completely fitted over the frequency range from  $350 \text{ cm}^{-1}$  to  $6\,000 \text{ cm}^{-1}$  and with increasing temperature up to 2 360 K in the case of  $\text{Al}_2\text{O}_3$  and 2 560 K in the case of  $\text{MgO}$ . The simulation is based on a semi-quantic dielectric function model with a classical Debye relaxation term used for the first time to fit the anomalous increase of the emissivity observed several degrees before melting within the transparency region. The results show that the model allows reproducing the experimental curves perfectly at any wavenumber and any temperature. The multiphonon processes are fitted as a temperature and frequency dependence of the damping function of the phonons and are proved to be significant only up to  $3\,500 \text{ cm}^{-1}$ . At higher frequency the dielectric strength of the relaxation term appears to be thermally activated and exhibits two behaviors in the case of  $\text{Al}_2\text{O}_3$ . These two different thermally activated behaviors are the consequence of a premelting range of about one hundred degrees. A comparison between the activation energies suggests that the cause of the phenomenon is the same for  $\text{MgO}$  as well as for  $\text{Al}_2\text{O}_3$ . The values of the characteristic frequency of the relaxation appear to be very high, included between 2 500 and 10 000  $\text{cm}^{-1}$ , which incites us to link it to a phenomenon at much higher frequency such as electronic transitions. These results and conclusions are to be completed with measurements and analysis of the normal spectral emissivity of  $\text{SiC}$  and  $\text{LiNbO}_3$  single crystals and  $\text{Ca}_2\text{SiO}_3$  glass.

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